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Request  
for  
Continued Examination (RCE)  
TransmittalAddress to:  
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P.O. Box 1450  
Alexandria, VA 22313-1450

Application Number	10727.700
Filing Date	12/04/2003
First Named Inventor	Zhenan Bao
Art Unit	2814
Examiner Name	Douglas A. Wille
Attorney Docket Number	BAO 39

This is a Request for Continued Examination (RCE) under 37 CFR 1.114 of the above-identified application. Request for Continued Examination (RCE) practice under 37 CFR 1.114 does not apply to any utility or plant application filed prior to June 8, 1995, or to any design application. See Instruction Sheet for RCEs (not to be submitted to the USPTO) on page 2.

1. **Submission required under 37 CFR 1.114** Note: If the RCE is proper, any previously filed unentered amendments and amendments enclosed with the RCE will be entered in the order in which they were filed unless applicant instructs otherwise. If applicant does not wish to have any previously filed unentered amendment(s) entered, applicant must request non-entry of such amendment(s).a. ☐ Previously submitted. If a final Office action is outstanding, any amendments filed after the final Office action may be considered as a submission even if this box is not checked.I. ☐ Consider the arguments in the Appeal Brief or Reply Brief previously filed on \_\_\_\_\_II. ☐ Other \_\_\_\_\_b. ☒ EnclosedI. ☐ Amendment/ReplyIII. ☒ Information Disclosure Statement (IDS)II. ☐ Affidavit(s)/Declaration(s)IV. ☐ Other \_\_\_\_\_2. **Miscellaneous**a. ☐ Suspension of action on the above-identified application is requested under 37 CFR 1.103(c) for a

period of \_\_\_\_\_ months. (Period of suspension shall not exceed 3 months; Fee under 37 CFR 1.17(i) required)

b. ☐ Other \_\_\_\_\_3. **Fees**The RCE fee under 37 CFR 1.17(e) is required by 37 CFR 1.114 when the RCE is filed. The Director is hereby authorized to charge the following fees, any underpayment of fees, or credit any overpayments, to Deposit Account No. 08-2395. I have enclosed a duplicate copy of this sheet.a. ☒ RCE fee required under 37 CFR 1.17(e)b. ☐ Extension of time fee (37 CFR 1.133 and 1.17)c. ☐ Other \_\_\_\_\_d. ☐ Check in the amount of \$ \_\_\_\_\_ enclosede. ☐ Payment by credit card (Form PTO-2038 enclosed)

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Signature	<i>Ronald J. Corbett</i>	Date	6/29/05	06/20/2005
Name (Print/Type)	Ronald J. Corbett	Registration No.	47,500	

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Signature	<i>Marty Bello</i>	Date	06/20/2005
Name (Print/Type)	Marty Bello		

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NO. 1639 P. 2  
PATENT

PATENT AND TRADEMARK OFFICE

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant: Zhenan Bao, et al. 275 USC - 371 3-15  
Serial No.: 10/727,709  
Filed: December 4, 2003  
Title: ORGANIC FIELD EFFECT TRANSISTORS WITH ACTIVE CHANNELS  
FORMED OF DENSIFIED LAYERS  
Group Art Unit: 2814  
Examiner: Waising Louie

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Date of Mailing

Marty Balko  
Signature of person mailing

Sir:

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On June 30, 2005 we filed an RCE and Foreign Search Information Disclosure Statement via facsimile to the USPTO in connection with the above-referenced case (see Attachment A). As you can see, on our Deposit Account Statement of July 2005 (see Attachment B), we were charged twice for the RCE fee: once on July 12, 2005 and the second time on July 22, 2005. We therefore request that the refund of the second RCE fee of \$790.00 which was withdrawn from the deposit account be refunded to our deposit account 082395.

Respectfully submitted,

HITT GAINES, P.C.

Ronald J. Corbett  
Ronald J. Corbett  
Reg. No. 47,500

Date: August 3, 2005  
Hitt Gaines, P.C.  
P.O. Box 832570  
Richardson, Texas 75083-2570  
(972) 480-8800

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P. 1

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Examiner Douglas A. Wille; Art Unit 2814

FAX NO. (571) 273-1721 (direct fax number for Examiner Wille)

FROM: Ronald J. Corbett

RE: Serial No.: 10/727,709  
Attorney Docket No.: BAO 39  
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DATE: June 30, 2005

PAGES: 13 (including cover page)

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Marty Balko  
(assistant to Ron Corbett)

Mailing Address: P.O. Box 832570, Richardson, Texas 75083-2570  
Street Address: Palisades Central II, 2435 North Central Expressway, Suite 1300, Richardson, Texas 75080-2753 U.S.A.  
Tel: (972) 480-8800 Fax: (972) 480-8865 [firm@hittgaines.com](mailto:firm@hittgaines.com)

#### Attachment A

PAGE 3/17 \* RCVD AT 8/3/2005 6:57:00 PM [Eastern Daylight Time] \* SVR:USPTO-EFAXF-6/25 \* DNIS:2738300 \* CSID:972 480 8865 \* DURATION (mm-ss):05:42

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Marty Balko

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Request  
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Transmittal

Address to:  
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P.O. Box 1450  
Alexandria, VA 22313-1450

Application Number	10/727,709
Filing Date	12/04/2003
First Named Inventor	Zhenan Bao
Art Unit	2814
Examiner Name	Douglas A. Wille
Attorney Docket Number	BAO 39

This is a Request for Continued Examination (RCE) under 37 CFR 1.114 of the above-identified application. Request for Continued Examination (RCE) practice under 37 CFR 1.114 does not apply to any utility or plant application filed prior to June 8, 1995, or to any design application. See Instruction Sheet for RCEs (not to be submitted to the USPTO) on page 2.

1. **Submission required under 37 CFR 1.114** Note: If the RCE is proper, any previously filed unentered amendments and amendments enclosed with the RCE will be entered in the order in which they were filed unless applicant instructs otherwise. If applicant does not wish to have any previously filed unentered amendment(s) entered, applicant must request non-entry of such amendment(s).

a. ☐ Previously submitted. If a final Office action is outstanding, any amendments filed after the final Office action may be considered as a submission even if this box is not checked.

i. ☐ Consider the arguments in the Appeal Brief or Reply Brief previously filed on \_\_\_\_\_  
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b. ☒ Enclosed

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ii. ☐ Affidavit(s)/ Declaration(s)

iii. ☒ Information Disclosure Statement (IDS)

iv. ☐ Other \_\_\_\_\_

2. **Miscellaneous**

a. ☐ Suspension of action on the above-identified application is requested under 37 CFR 1.103(c) for a period of \_\_\_\_\_ months. (Period of suspension shall not exceed 3 months; Fee under 37 CFR 1.17(i) required)

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3. **Fees**

The RCE fee under 37 CFR 1.17(e) is required by 37 CFR 1.114 when the RCE is filed.

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Name (Print/Type)	Ronald J. Corbett	Registration No.	47,500	

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PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of:

Zhenan Bao

Serial No.: 10/727,709

Filed: December 4, 2003

For: ORGANIC FIELD EFFECT TRANSISTORS WITH ACTIVE CHANNELS  
FORMED OF DENSIFIED LAYERS

Group No.: 2811

Examiner: Douglas A. Wille

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Marta Balko  
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Date of Mailing

Marta Balko  
Signature of person mailing

Sir:

FOREIGN SEARCH INFORMATION DISCLOSURE STATEMENT

In accordance with 37 C.F.R. §1.56 and the provisions of 37 C.F.R. §§1.97 and 1.98 and §609 of the Manual of Patent Examining Procedure, Applicant hereby makes a disclosure of the patents, publications and other information listed below and on the accompanying form IDS by Applicant, which may be potentially material to the patentability of the invention disclosed in the above-referenced application. Pursuant to § 1.97(e) the Applicant hereby states that each item of information contained in the information disclosure statement was cited in a communication from a

foreign patent office in a counterpart foreign application not more than three months prior to the filing of the information disclosure statement.

U.S. Patent No.

Inventor

Date

5,546,889

Wakita, et al.

August 20, 1996

Other References:

YU-TAITAO, et a. "Structure Evolution of Aromatic-Derivatized Thiol Monolayers on Evaporated Gold", Langmuir, Volume 13, No. 15 (1997), pages 4018-4023.

As attorney for the Applicant, I am signing below on the basis of the information supplied by an individual designated in § 1.56(c).

The Commissioner is hereby authorized to charge any fees or credit any overpayments to Deposit Account No. 08-2395.

Respectfully submitted,

HITT GAINES, P.C.



Ronald J. Corbett  
Registration No. 47,500

Date: June 30, 2005

Hitt Gaines, P.C.  
P.O. Box 832570  
Richardson, Texas 75083-2570  
(972) 480-8800

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(Use as many sheets as necessary)

Sheet

1

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2

**Complete If Known**

Application Number	10727709
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Filing Date	December 4, 2003
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First Named Inventor	Zhenan Bao
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Art Unit	2811
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Examiner Name	Douglas A. Wille
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Attorney Docket Number	BAO-39
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[illegible][illegible]

Examiner Signature		Date Considered	
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# Structure Evolution of Aromatic-Derivatized Thiol Monolayers on Evaporated Gold

Yu-Tai Tao,\* Chien-Ching Wu, Ji-Yang Eu, and Wen-Ling Lin

Institute of Chemistry, Academia Sinica, Taipei, Taiwan, Republic of China

Kwang-Chen Wu and Chun-hsien Chen\*

Department of Chemistry, National Sun Yat-Sen University, Kaohsiung, Taiwan 80424, Republic of China

Received January 31, 1997; In Final Form May 12, 1997

The structure of self-assembled monolayers of thiophenols (I), benzyl mercaptans (II), biphenylthiols (III), and 4-biphenylmethanethiols (IV) on the surface of Au(111) are compared using cyclic voltammetry, reflection absorption infrared spectroscopy, scanning tunneling microscopy, ellipsometry and contact angle measurement. The results suggest that benzyl mercaptans and 4-biphenylmethanethiols form closely packed and ordered monolayer, irrespective of the length of a *p*-alkoxy substituent. For thiophenol and biphenylthiol, a film of lower surface coverage was formed. A long *p*-alkoxy chain (*n*-C<sub>18</sub>H<sub>37</sub>O) increases the intermolecular interaction and leads to a closer packing within the monolayer film. The difference is attributed to the interplay between intermolecular interaction and the bond angle preference at the thiolate head group.

## Introduction

The self-assembling of organothiol on gold to form a monolayer has attracted much attention lately both from the fundamental point of view and from their application prospects.<sup>1</sup> In these applications, structural order and integrity of the film are of major concern. A simple alkanethiol monolayer is one of the most thoroughly studied self-assembled monolayer (SAM) systems. Detailed structural information regarding the packing, orientation, as well as conformation of the molecular chains have been accumulated by various analytical techniques.<sup>2-4</sup> The aromatic-containing monolayer is of importance because many optoelectronic applications involve an aromatic chromophore as the functioning unit. Many studies of aromatic-containing monolayers on gold have been reported, with the aromatic moiety as the only major component or as a part of a chain or in the presence of other functional groups.<sup>5-7</sup> It has been shown that such molecules anchor on gold substrates predominantly

through the sulfur atom instead of the aromatic ring.<sup>8</sup> Nevertheless, a variety of structural details are proposed. It is noted that for the simplest member of the arylthiol, thiophenol, the detailed structure has not been unambiguously determined. On the basis of several methods, Sabatani *et al.*<sup>9</sup> concluded that thiophenol forms poorly defined monolayers. Well-ordered lattice structure was not found by high-impedance scanning tunneling microscopy (STM) for thiophenol monolayer either.<sup>10</sup> With an increase of the number of aromatic moieties, the monolayers become either more densely packed or well ordered,<sup>11,12</sup> presumably a result of stronger adsorbate-adsorbate interactions. The effect of a pending alkyl chain on the packing is not well understood.<sup>13,14</sup>

In this paper we wish to report our further structural studies for monolayers formed by a series of aromatic-derivatized thiols, namely, I-IV (Chart 1), on gold in order

\* Abstract published in Advance ACS Abstracts, June 15, 1997.

(1) For a general review, see: (a) Ulman, A. *An Introduction to Ultrathin Organic Films*; Academic Press: Boston, MA, 1991. (b) Ulman, A. *Chem. Rev.* 1996, 96, 1533-1554.

(2) Porter, M. D.; Bright, T. S.; Allara, D. L.; Chidsey, C. E. D. *J. Am. Chem. Soc.* 1987, 109, 3559-3558.

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(9) (a) Strong, L.; Whitesides, G. M. *Langmuir* 1988, 4, 546-559. (b) Dubois, L. H.; Ziegler, B. R.; Nuzzo, R. G. *J. Chem. Phys.* 1989, 90, 678-682. (c) Porter, P.; Eisenberg, P.; Li, J.; Camillone, N.; Whitesides, G. M.; Nuzzo, R. G.; Penner, M. O.; Brown, C. A.; Gordon, J. G. *Langmuir* 1991, 7, 2013-2016. (d) Strohriem, M. O.; Brown, C. A.; Gordon, J. G. *Langmuir* 1991, 7, 497-499. (e) Chidsey, C. E. D.; Liu, C.; Ruckenstein, P.; Seol, G. *J. Chem. Phys.* 1988, 87, 4421-4423.

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(14) Kwan, W. S. V.; Arakawa, L.; Miller, L. L. *Langmuir* 1991, 7, 1418-1428.

(15) Dpirani, A.; Zehner, R. W.; Huang, R. P.; Guyot-Stonnest, P.; Shih, L. R. *J. Am. Chem. Soc.* 1995, 117, 5316-5320.

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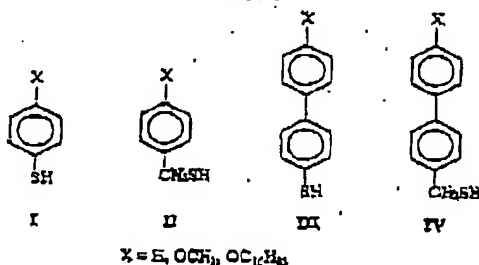
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## Structure Evolution of Thiol Monolayers

Chart 1



to delineate factors that determine the structural order. Here the adsorbate-adsorbate interaction is manipulated in two ways. First, along the line of aforementioned packing promoted by intermolecular attractions, we systematically examine monolayer structures as a function of the number of rings involved and the length of the alkyl chain connected to the ring. Second, we perturb the steric conformation of head groups by inserting one methylene unit in between the aryl and the mercapto group (i.e., compounds II and IV). The results show, for the first time, that the insertion of the methylene unit can turn ill-defined thiophenol monolayers into well-ordered SAMs of benzyl mercaptans. In addition, depending on the length of a para-substituted alkoxy group, various structural order and packing density were obtained for thiophenol. A simulation model derived by Sellers *et al.*<sup>10</sup> is adopted to elucidate the discrepancy arising from the insertion of the methylene unit. The different behavior is attributed to a counterbalance of intermolecular interaction and bond angle preference at the sulfur atom ( $sp^3$  versus  $sp$ ).

## Experimental Section

**Materials.** Thiophenol, ethyl mercaptan, and benzyl mercaptan were obtained from Aldrich and used directly. 4-Methoxybenzyl mercaptan, 4-biphenylmethanethiol, (4,4'-methoxybiphenyl)methanethiol and (4,4'-(hexadecyloxy)biphenyl)methanethiol were prepared by thioether substitution of corresponding benzylic bromides followed by hydrolysis.<sup>21</sup> The 4-biphenylthiol and 4,4'-methoxybiphenylthiol were synthesized from corresponding aryl bromide by metal-halogen exchange followed by sulfur quench. 4,4'-(Hexadecyloxy)biphenylthiol was prepared by sodium ethanethiolate substitution of the corresponding bromide followed by selective dealkylation of the resulting thioether.<sup>24</sup>

**Substrate Preparation.** The gold substrates were prepared by vapor deposition of about 200 nm of gold (99.99% purity) onto freshly cleaved 1-in. mica sheets at a rate of 1 nm/s under a pressure of  $9 \times 10^{-7}$  Torr using an Ulvacryo-pumped evaporator. The vacuum chamber was back-filled with high-purity nitrogen after 45 min after deposition. The gold substrates were transferred to a furnace and annealed at 300 °C for 4 h. The roughness factor for substrates prepared under these condition was estimated to be 1.2.<sup>25</sup> The gold electrodes were cleaned in a UV ozone cleaner for 1 h and washed with ethanol right before these substrates were immersed in thiol solution. For IR measurement, 2-in. silicon wafers were used as the substrate in gold deposition. An adhesion layer of chromium (5–10 nm) was deposited before gold evaporation.

**Monolayer Preparation.** Thiols with one phenyl ring are dissolved in ethanol in a concentration of 1 mM. Compounds

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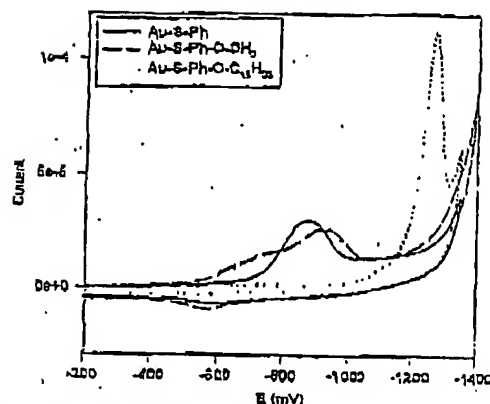


Figure 1. Cyclic voltammograms for Au-S-C<sub>6</sub>H<sub>5</sub>, Au-S-C<sub>6</sub>H<sub>4</sub>-O-CH<sub>3</sub>, and Au-S-C<sub>6</sub>H<sub>4</sub>-O-C<sub>12</sub>H<sub>25</sub> monolayers.

containing two aromatic rings are less soluble and were first dissolved in a minimum amount of THF, and then ethanol was added to make up the final solution of 0.25 mM. Substrates were immersed in solution for at least 24 h. Samples were washed with THF and ethanol successively and dried with a flow of argon gas or spun-dried prior to use.

**Electrochemical Measurement.** A CV-27 potentiostat or a 300S electroanalysis system (Bioanalytical Systems, West Lafayette, IN) was used in cyclic voltammetry measurements. A conventional three-electrode cell was used with the area of the working electrode defined by the opening in an inert elastomer O-ring (0.56 cm<sup>2</sup>). A Pt coil auxiliary electrode and an Ag/AgCl/5 M NaCl reference electrode were used; all voltages were recorded with respect to this reference electrode. The supporting electrolyte was 0.5 M KOH (99.99% purity) in distilled, deionized water. The solution was purged with argon for 10 min prior to the experiment. The applied potential was cycled between -0.2 and -1.95 V at a scan rate of 100 mV/s with an initial potential of -0.2 V.

**STM Measurements.** STM measurements were carried out with a NanoScope II (Digital Instruments, Santa Barbara, CA) using a commercial Pt/Ir tip or a tungsten tip which was electrochemically etched in 1 M KOH. The images were calibrated by imaging Au(111) or HOPG (highly oriented pyrolytic graphite) in air.

Details of infrared measurements, ellipsometry measurements, and contact angle measurement were described previously.<sup>10</sup>

## Results

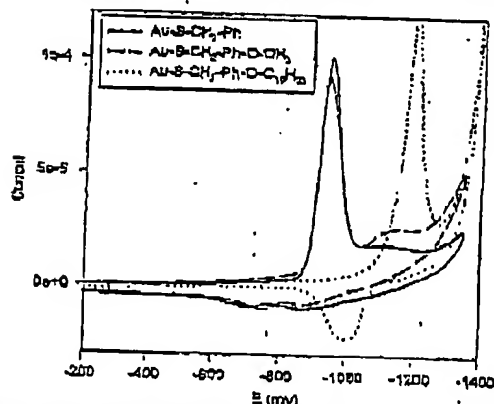
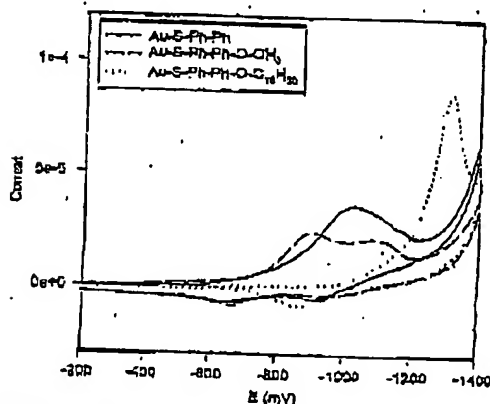
**Electrochemical Measurement.** The typical linear sweep voltammograms for the four series of monolayers on Au are shown in Figures 1–4. A summary of the desorption peak potentials and calculated surface coverages is shown in Table 1. In general, the peak on the reductive scan represents the desorption of the monolayer from the gold electrode. The area under the peak relates the number of molecules that were reductively desorbed from the surface as thiolate assuming a one-electron reduction process<sup>26</sup> and is directly related to the surface coverage. The peak potential has been shown to depend on the hydrocarbon chain length of the thiolate and such dependence is suggested to be related to the potential required to establish a potential gradient through the film that induces an ion flux sufficient to support the reduction process. It is noted that for the series II and IV, all the desorption peaks are rather sharp and well defined, whether it is unsubstituted or substituted with alkoxy group of different length. Moreover, the surface

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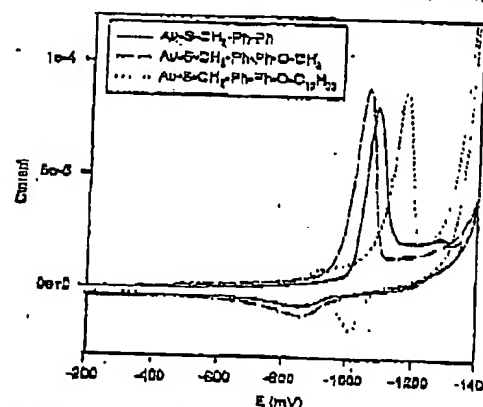
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Table 1. Packing Density ( $\times 10^{-10}$  mol/cm<sup>2</sup>) and the Desorption Potential (mV) in Parentheses of Aromatic-Derived Thiols on Evaporated Au Using Electrochemically Reductive Desorption Method

	I	II	III	IV
X = H	4.4 $\pm$ 0.4 (-848)	5.1 $\pm$ 0.3 (-921)	5.1 $\pm$ 0.7 (-926)	8.0 $\pm$ 0.3 (-1081)
X = OCH <sub>3</sub>	5.1 $\pm$ 0.5 (-921)	4.1 $\pm$ 0.3 (-939)	5.4 $\pm$ 0.8 (-907)	8.0 $\pm$ 0.1 (-1037)
X = OC <sub>18</sub> H <sub>35</sub>	6.6 $\pm$ 0.6 (-1216)	8.0 $\pm$ 0.4 (-1152)	7.7 $\pm$ 0.3 (-1305)	7.5 $\pm$ 0.3 (-1167)

Figure 2. Cyclic voltammograms for Au-S-CH<sub>2</sub>-C<sub>6</sub>H<sub>5</sub>, Au-S-CH<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>-O-CH<sub>3</sub>, and Au-S-CH<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>-O-C<sub>18</sub>H<sub>35</sub> monolayers.Figure 3. Cyclic voltammograms for Au-S-C<sub>6</sub>H<sub>5</sub>-C<sub>6</sub>H<sub>5</sub>, Au-S-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-O-CH<sub>3</sub>, and Au-S-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-O-C<sub>18</sub>H<sub>35</sub> monolayers.

coverages as calculated from the area under the peaks are similar irrespective of the substituent group on the aromatic ring. And the value is also close to that for the saturated *n*-hexadecanethiolate monolayer on gold,  $7.8 \times 10^{-10}$  mol/cm<sup>2</sup>, equivalent to  $21.3 \text{ \AA}^2/\text{molecule}$ . For *n*-hexadecanethiolate monolayer, an overlayer of  $(\sqrt{3} \times \sqrt{3})\text{R}30^\circ$  was shown by various methods, and a packing density of  $7.7 \times 10^{-10}$  mol/cm<sup>2</sup> ( $21.6 \text{ \AA}^2/\text{molecule}$ ) is expected for such an overlayer.<sup>10</sup> Thus compounds in these two series most likely occupy a similar lattice as that of *n*-hexadecanethiolate monolayer. The desorption peak potential shows a trend to become more negative with increasing substituent chain length in the same series. The trend is more significant for the monophenyl system

Figure 4. Cyclic voltammograms for Au-S-CH<sub>2</sub>-C<sub>6</sub>H<sub>5</sub>, Au-S-CH<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-O-CH<sub>3</sub>, and Au-S-CH<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-O-C<sub>18</sub>H<sub>35</sub> monolayers.

(~240 mV difference in going from unsubstituted or methoxy-substituted to hexadecyloxy substituted) than the biphenyl system (~100 mV for the corresponding change). These are consistent with the increasing difficulty in the penetration of ions through the film during reduction.<sup>11</sup> The shorter (monophenyl) system is more sensitive to the addition of shielding layer than the longer (biphenyl) system. The desorption peak potential is also more negative for the biphenyl series than the monophenyl series, with the same substituent group. The trend again is more significant for short chain (or unsubstituted) derivatives than the long chain derivatives.

On the other hand, for series I and III, the desorption peak shapes for the unsubstituted and methoxy-substituted ones are rather broad and ill-defined. More than one peak was also observed. Only with the C18-substituted ones, a sharper and well-defined curve was obtained. The packing density depends very much on the substituent group on the aromatic ring, ranging from  $4.4 \times 10^{-10}$  mol/cm<sup>2</sup> ( $37.8 \text{ \AA}^2/\text{molecule}$ ) for thiophenol to  $8.6 \times 10^{-10}$  mol/cm<sup>2</sup> ( $25.2 \text{ \AA}^2/\text{molecule}$ ) for hexadecyloxy-substituted thiophenol. With the biphenyl system, the packing density increases from  $5.1 \times 10^{-10}$  mol/cm<sup>2</sup> ( $32.6 \text{ \AA}^2/\text{molecule}$ ) for the unsubstituted one to  $7.7 \times 10^{-10}$  mol/cm<sup>2</sup> ( $21.6 \text{ \AA}^2/\text{molecule}$ ) for the hexadecyloxy-substituted one. Thus for monolayers of series I and III with X = H, the coverages are only about 60% of that of a full  $(\sqrt{3} \times \sqrt{3})\text{R}30^\circ$  monolayer, implying each molecule is occupying a larger coverage area than in the corresponding case of II and IV. With increasing chain length of the substituent, the packing becomes denser. It is further noted that the desorption peak potentials do not differ by much between series I and III for the same substituent group, except for the long chain substituted one. This is in opposite trend as that observed for series II and IV, which could imply that the aromatic groups did not pack well in the adsorbed state to block the flux of ions during the reduction.

Infrared Reflection Absorption Spectra. Reflection-absorption IR spectra of monolayers of the four series

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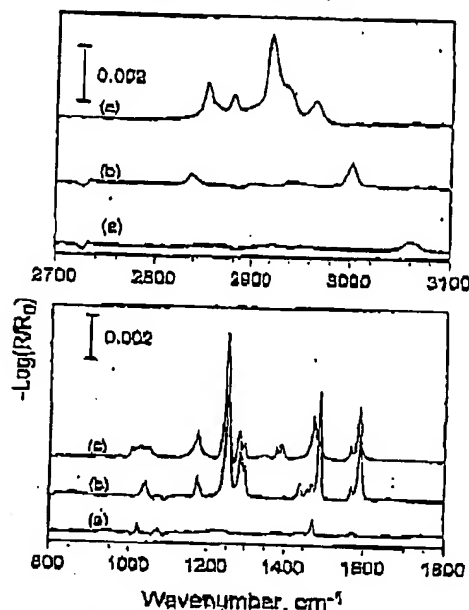


Figure 5. Infrared reflection absorption spectra for (a) Au-S-C<sub>6</sub>H<sub>5</sub>, (b) Au-S-C<sub>6</sub>H<sub>4</sub>-O-CH<sub>3</sub>, and (c) Au-S-C<sub>6</sub>H<sub>4</sub>-O-C<sub>6</sub>H<sub>5</sub> monolayers.

Table 2. Infrared Ring-Stratifying Frequency of Aromatic-Substituted Thiols on Evaporated Au and the Shift from Corresponding Value in KBr Sample, cm<sup>-1</sup>

	I	II	III	IV
X = H	1472, -6	1494, 0	1475, -8	1488, 2
X = OCH <sub>3</sub>	1488, -7	1518, 8	1479, -7	1501, 0
X = OC <sub>6</sub> H <sub>5</sub>	1488, -9	1514, 1	1473, 0	1501, 0

of compounds were taken. A representative series (for compound I) is shown in Figure 5. (The others are supplied as Supporting Information.) In general, the peak patterns in the C-H stretching region are very similar for the same substituent. Thus for C<sub>16</sub> substituted cases, the peak positions for methylene stretches (at 2918 and 2850 cm<sup>-1</sup>) respectively for II and shifted less than 2 cm<sup>-1</sup> to higher end for the other three series) indicate close packing, if not a perfectly crystalline state of the chains. There are some variations in the relative intensities, which should be dependent on the exact chain tilt and twist. The methoxy-substituted ones all exhibit the same intensity for  $\nu_a(\text{OCH}_3)$  at around 3062 cm<sup>-1</sup> and  $\nu_s(\text{OCH}_3)$  around 2880 cm<sup>-1</sup>. The only major feature for the unsubstituted ones is a weak band around 3082 cm<sup>-1</sup>, which is assigned as the aromatic C-H stretch. In the low-frequency region, of particular interest is the peak positions for the ring stretch mode occurring at around 1472–1515 cm<sup>-1</sup> when compared to the KBr spectra of isotropic sample. The stretching frequency of the aromatic ring of monolayers I and III on Au shifted to lower values (by 5–9 wave-numbers) as compared to that in KBr spectra, except with X = C<sub>16</sub> for III, whereas for monolayers of II and IV there is no change or a slightly positive shift in this ring-stretching frequency as compared to that in the KBr spectra (Table 2). The implication of these trends will be discussed later.<sup>11</sup>

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Table 3. Ellipsometric Thicknesses of Aromatic-Substituted Thiol Monolayers on Evaporated Au (Å)

	I	II	III	IV
X = H	1.3	2.4	9.4	10.3
X = OCH <sub>3</sub>	1.8	5.2	10.4	13.9
X = OC <sub>6</sub> H <sub>5</sub>	22.3	28.2	30.6	33.3

Scanning Tunneling Microscopy Measurement. STM measurements show that the annealed bare gold substrates exhibit smooth plateaus with average size of ca. 50 nm in width. Images obtained on plateaus and terraces are composed of hexagonally close packed atoms with nearest-neighbor spacing of  $2.38 \pm 0.3$  Å, indicative of Au(111) orientation. All four series of thiols significantly affect the substrates, resulting in morphological features of pits and jagged step edges which are characteristic of  $\alpha$ -alkanethiol monolayers on gold.<sup>14,25</sup> Because of the concerns of monolayer structures interfering with the STM tip due to the less conductive long alkyl chains, our report will concentrate on unsubstituted ones (X = H).

For monolayers of benzyl mercaptan (II), STM images always display a highly ordered hexagonal pattern. Figure 6a is a representative image obtained with 2 GΩ tunneling impedance (a bias voltage and tunneling current of 1.0 V and 0.5 nA, respectively). Under this condition, there is no indication of destructive imaging. Only one lattice structure is observed. The unit cell dimension is  $4.9 \pm 0.1$  Å and the angle between lattice vectors is  $55 \pm 5^\circ$ , consistent with a  $(\sqrt{3} \times \sqrt{3})\text{R}30^\circ$  structure. The dark defect shown in the image also exhibits the same lattice parameters which can be seen clearly by adjusting the image contrast. For monolayers of 4-biphenylmethanethiol (IV), the adlayer adopts preferentially a  $(\sqrt{3} \times \sqrt{3})\text{R}30^\circ$  structure, although an unassigned local structure is also found.<sup>26</sup> A typical image of the  $(\sqrt{3} \times \sqrt{3})\text{R}30^\circ$  structure is presented in Figure 6b, which was obtained with 1 GΩ tunneling impedance. We notice that the imaging quality of series IV is, in general, not as decent as that of benzyl mercaptan (II). The origin of this difference is probably arising from the fact that the tunneling barrier of IV monolayers is an aryl ring thicker than those of II.

In contrast, for monolayers of series I and III with X = H and OCH<sub>3</sub>, neither periodic pattern nor molecularly resolved images are observed, coherent with the finding of a previous STM study by Dhirani *et al.*<sup>16</sup> In the case of (hexadecyloxy)phenylthiol (I with OC<sub>16</sub>H<sub>33</sub>), we observed a  $(\sqrt{3} \times \sqrt{3})\text{R}30^\circ$  overlayer in only a few occasions. The domain size is as small as ca. 4 nm. The film structure appears predominantly disordered.

**Ellipsometric Thickness Measurement.** The ellipsometric thicknesses of these monolayers are collected in Table 3. Qualitatively, the benzyl mercaptan derivatives (II and IV) are thicker, when compared with thiophenol analogues (I and III), presumably because of the additional CH<sub>2</sub> unit in the benzyl mercaptan system. The biphenyl systems (III and IV) are also thicker when

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(23) We have observed a local structure exhibiting stripe modulation running across pits and line defects. The nearest-neighbor spacings along two primitive unit cell vectors are  $4.0 \pm 0.4$  and  $5.0 \pm 0.3$  Å and the angle between the vectors is  $88 \pm 7^\circ$ . Although the pattern looks like a rectangular  $p \times \sqrt{3}$  structure, the area of the unit cell is too small to be the high-millimetry. At the present time, we are unable to assign a commensurate structure for this adlayer.

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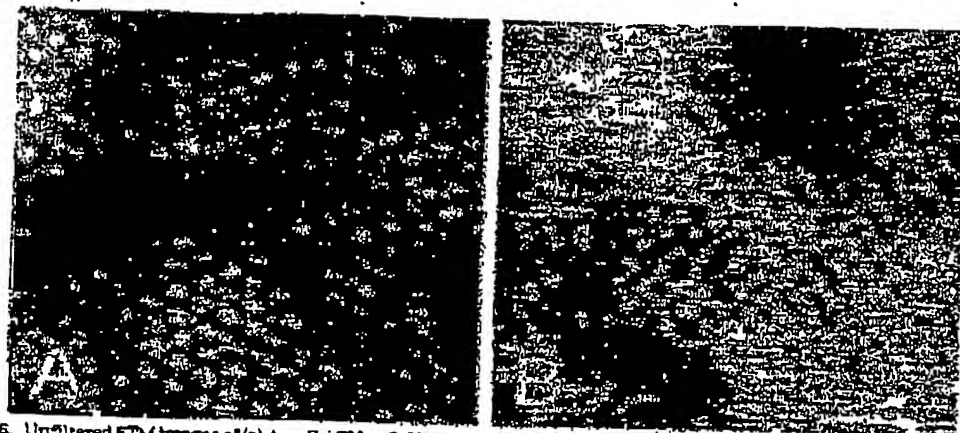


Figure 6. Unfiltered STM images of (a) Au-S-CH<sub>2</sub>-C<sub>6</sub>H<sub>5</sub> (image size 8 × 8 nm,  $I_t = 0.3$  nA,  $V_{bias} = 1.0$  V, nearest-neighbor spacing  $4.9 \pm 0.1$  Å) (b) Au-S-CH<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>5</sub> (image size 8 × 8 nm,  $I_t = 0.5$  nA,  $V_{bias} = 600$  mV, nearest-neighbor spacing  $4.9 \pm 0.3$  Å).

Table 4. Contact Angle (deg) of H<sub>2</sub>O on the Aromatic-Derivatized Thiol Monolayers on Evaporated Au

	I	II	III	IV
X = H	70	63	80	89
X = OCH <sub>3</sub>	88	84	50	66
X = OC <sub>6</sub> H <sub>5</sub>	109	112	112	111

compared with monophenyl analogues (I and II), as one would expect for the additional phenyl group in the biphenyl system. However, in an absolute sense, the observed thicknesses for the unsubstituted or short-chain substituted ones are thinner than the expected values from the dimension of the molecules involved. Furthermore, the difference between each series is more than that expected for the group involved (1.4 Å for a CH<sub>3</sub> group and 7 Å for a phenyl group). These may be due to the uncertainty associated with ellipsometry measurement (index of refraction, surface contamination on "bare" gold  $\lambda$ ) as well as different packing density in each series, as evidenced by the electrochemical data. The ellipsometry data here can only serve as a qualitative support of the "monolayer" nature of the adsorbed film.

**Contact Angle Measurement.** Water contact angle values are reported in Table 4. It can be seen that the water contact angles on II and IV monolayers are higher than those on the analogues in I and III, but the difference decreases with increasing the length of X. While it can be argued that as the substituent chain length increases, the contact angle is less sensitive to the underlying substrate. It could also imply that the difference in the structure between I and II (or III and IV) diminishes as X increases in chain length.

#### Discussion

The data appear to fall into two categories. The first category includes benzyl mercaptans (II) and 4-biphenylmethanethiols (IV), both of which have a CH<sub>2</sub> unit between the thiol head group and the aromatic ring. They give well-defined cyclic voltammetry behavior in that the reductive wave is sharp and more uniform. The coverages correspond well to that of a close-packed *n*-alkanethiol monolayer. These adsorbates are expected to have a packing scheme similar to that of the *n*-alkanethiol, i.e.,  $\sqrt{3} \times \sqrt{3}$  R30° overlayer, as also evidenced by STM

measurements. The second category includes thiophenols and biphenylthiols. In contrast with benzyl mercaptans, both thiophenol and *p*-methoxythiophenol gave a rather broad desorption peak and low surface coverage, which implies a rather ill-defined film structure and lower packing density. This is in agreement with STM observations and literature reports<sup>12,11</sup> that thiophenol forms poor monolayers.<sup>14</sup>

The discrepancy between these two categories shows the significance of the inserted methylene unit. For compounds containing the methylene unit, II and IV, the  $(\sqrt{3} \times \sqrt{3})R30^\circ$  lattice structure suggests the herringbone packing of phenyl or biphenyl moieties. Considering the dimension of the phenyl ring,<sup>21</sup> a herringbone packing will require the aromatic planes orienting nearly vertical to the gold surface.<sup>12</sup> This geometry was also suggested for adsorption of dibenzyl disulfide on silver<sup>21</sup> where the phenyl ring is "sticking up". For compounds without the methylene unit, I and III, the negative shifts in the IR frequency of the ring stretch mode region (from 1472 to 1515 cm<sup>-1</sup>) are similar to that observed in the adsorption of diphenyl disulfide on silver,<sup>21</sup> where a "lying-flat" geometry was proposed based on Raman spectroscopy. This negative shift suggests that the long axis of the benzene ring (the one passing through X and S) for compounds I and III is inclined toward the gold surface. This tilt creates steric hindrance which would occupy a larger space and diminish intermolecular attractions between neighboring phenyl rings, and thus results in a poorly defined monolayer. Given the resemblance of these compounds, the methylene unit is an intriguing factor in orienting the phenyl ring vertical to the surface.

The critical role of the methylene unit can be illustrated by an S-Ar binding scheme modeled by the quantum calculations of Sellers et al.<sup>20</sup> who proposed sp and sp<sup>3</sup> hybridization with surface-S-C bond angles of 180° and 104°, respectively. In the case of saturated *n*-alkanethiol on Au(111), the trend in the odd-even effect observed in

(14) It is noted that a different conclusion was obtained for biphenylthiol from electron transfer rate measurement.<sup>12</sup> However, it is also noted in the same work that surface coverage measurements by ac impedance and gold oxide removal on a monolayer-covered surface indicated that biphenylthiol behaved more like thiophenol than arylthiols in the monolayer assembly.

(15) van der Waals dimensions of a vertically oriented phenyl ring are 5.4 Å (width) × 3.5 Å (thickness).



## Structure Evolution of Thiol Monolayers

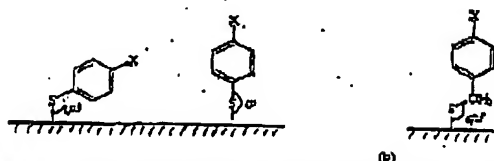


Figure 7. Possible orientation of monolayers of (a) thiophenol and (b) benzyl mercaptan derivatives on gold.

IR,<sup>6,7,10</sup> which reflecting the orientation of the terminal methyl group, clearly implies a preference of  $sp^3$  hybridization in the sulfur atom (or a bent Au-S-C bond angle) and a trans zigzag extension of the alkyl chain. A linear Au-S-C bond angle (or  $sp$  hybridization) has been invoked to rationalize a reversed trend in the odd-even effect observed on Ag.<sup>10</sup> In the case of compounds I and III with X = H and OCH<sub>3</sub>, the tilt orientation of phenyl ring implies that  $sp^3$  hybridization is more favorable than  $sp$  hybridization (Figure 7a). For compounds II and IV, in order to adopt the close-packed  $(\sqrt{3} \times \sqrt{3})R30^\circ$  structure, a bond angle of C-S-Au is required. Consequently,  $sp^3$  hybridization appears to be the favorable one for compounds II and IV as well (Figure 7 b). In either category, the S atom adopts  $sp^3$  hybridization when X = H or OCH<sub>3</sub>. Therefore, the insertion of a methylene unit can relax the rigidity of the thiol head group and lead to a stronger intermolecular interaction.

For compounds I and III with a long chain substituent, such as a hexadecyl group, the electrochemical behavior is approaching that of the benzyl mercaptans. The same IR pattern in the CH stretching region also implies similar packing and orientation in the long alkyl chain portion. This would compel the long ends of the benzene ring to point nearly perpendicular to the surface. This is achieved by a greater surface-S-C bond angle or, equivalently, the adoption of  $sp$  hybridization at the sulfur atom, with energy compensated by a greater interchain interaction.

*Langmuir*, Vol. 13, No. 15, 1997, 4023

## Conclusions

It is shown in this study that for phenyl-substituted thiols, the structure of a monolayer formed on gold is dependent on the location of the aromatic ring. With a methylene unit inserted between the phenyl ring and the thiol head group, a closely packed and ordered monolayer of  $(\sqrt{3} \times \sqrt{3})R30^\circ$  structure can be formed. The substituent at the para-position increases the interchain interaction but does not change grossly the packing density and/or arrangement. With a thiol group directly attached to the aromatic ring, the para-substituent affects the packing in the monolayer. In the absence of a substituent or in the presence of a short chain, a less densely packed monolayer with coverage as low as 60% of that of a fully packed monolayer can result. A longer chain introduces greater interchain interaction and results in a higher coverage. The difference between these two categories of thiols is suggested to be a balance of the interchain interaction and the bonding geometry adopted at the thiolate head group. An  $sp^3$  hybridization is suggested to be the favored state at the sulfur atom. This geometry allows the benzyl-type thiols to arrange the aromatic rings into a well-ordered packing but prohibit the thiophenol-type molecules to arrange their aromatic moiety. With a longer substituent at the para-position, greater packing interaction causes a change of bond angle (or a change of hybridization) to allow a tighter packing of the rings.

**Acknowledgment** Financial support from National Science Council, Republic of China, is gratefully acknowledged. C.H.C. gratefully acknowledges the Chemistry Department of National Sun Yat-sen University for a generous starting fund.

**Supporting Information Available:** Figures of infrared refraction absorbance spectra for II-IV monolayers (2 pages). Ordering information is given on any current masthead page.

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